

**Supporting Information:**  
**Gas-phase detection and rotational spectroscopy**  
**of ethynethiol, HCCSH**

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## Supporting Information Available

### Vibrational frequencies of HCCSH

Krantz and Lauren<sup>S1</sup> used argon matrix isolation to measure the infrared spectrum of HCCSH. As a point of reference, we provide a comparison of the *ab initio* gas-phase harmonic frequencies and intensities in Table S1. The frequencies are in very good agreement, and are systematically red-shifted due to interaction with the matrix as well as the lack of anharmonicity in our calculations. The intensities are also in agreement with the qualitative notation from Krantz and Lauren<sup>S1</sup>; the weak features have correspondingly low intensities in our calculation, and the same applies to the strongest feature in their spectrum at 3315 cm<sup>-1</sup>.

**Table S1: Comparison of the experimental assignments and noted intensity of infrared bands of HCCSH adapted from Krantz and Lauren<sup>S1</sup>, and the harmonic frequencies calculated at the ae-CCSD(T)/cc-pCVQZ level. The notation used for the matrix intensities are: very weak (vw), weak (w), medium (m), and strong (s). The three lowest frequency transitions have not been observed. Frequencies are given in cm<sup>-1</sup>, and intensity in km/mol.**

Argon matrix <sup>S1</sup>	Harmonic frequency	Harmonic intensity
3315 (s)	3468	72.8
2575 (vw)	2685	0.5
2065 (w)	2126	9.3
1112 (m)	977	12.7
959 (w)	718	0.4
558 (w)	696	33.2
	578	54.3
	352	6.3
	296	6.9

# Rotational transitions of HCCSH

In Table S2 we present the transition frequencies of HCCSH from 10 – 650 GHz. Cavity frequencies are obtained by fitting the Doppler-split transitions with a pair of Gaussian lineshapes, and calculating the arithmetic mean of the two centers. The DR frequencies are obtained by fitting a Gaussian distribution to the depletion. The millimeter/submillimeter frequencies are obtained by fitting second derivative Lorentzian line profiles to the spectral features.

**Table S2: Frequencies of observed transitions for HCCSH. Frequencies are given in MHz, and uncertainties correspond to  $1\sigma$ .**

$J' \rightarrow J''$	$K'_a \rightarrow K''_a$	$K'_c \rightarrow K''_c$	Frequency	Uncertainty
1 $\rightarrow$ 0	0 $\rightarrow$ 0	1 $\rightarrow$ 0	10985.9808	0.002
2 $\rightarrow$ 1	...	2 $\rightarrow$ 1	21971.8961	0.002
3 $\rightarrow$ 2	...	3 $\rightarrow$ 2	32957.6832	0.002
1 $\rightarrow$ 1	1 $\rightarrow$ 0	0 $\rightarrow$ 1	285955.7468	0.05
2 $\rightarrow$ 2	...	1 $\rightarrow$ 2	286064.3678	0.05
3 $\rightarrow$ 3	...	2 $\rightarrow$ 3	286227.3426	0.05
4 $\rightarrow$ 4	...	3 $\rightarrow$ 4	286444.6485	0.05
5 $\rightarrow$ 5	...	4 $\rightarrow$ 5	286716.5324	0.05
6 $\rightarrow$ 6	...	5 $\rightarrow$ 6	287042.9925	0.05
7 $\rightarrow$ 7	...	6 $\rightarrow$ 7	287424.2084	0.05
8 $\rightarrow$ 8	...	7 $\rightarrow$ 8	287860.38	0.05
9 $\rightarrow$ 9	...	8 $\rightarrow$ 9	288351.6016	0.05
10 $\rightarrow$ 10	...	9 $\rightarrow$ 10	288898.1146	0.05
11 $\rightarrow$ 11	...	10 $\rightarrow$ 11	289500.1769	0.05
12 $\rightarrow$ 12	...	11 $\rightarrow$ 12	290158.0034	0.05
13 $\rightarrow$ 13	...	12 $\rightarrow$ 13	290871.8486	0.05

$J' \rightarrow J''$	$K'_a \rightarrow K''_a$	$K'_c \rightarrow K''_c$	Frequency	Uncertainty
14 → 14	...	13 → 14	291642.0966	0.05
15 → 15	...	14 → 15	292469.0325	0.05
16 → 16	...	15 → 16	293352.7731	0.05
17 → 17	...	16 → 17	294294.0508	0.05
18 → 18	...	17 → 18	295293.0033	0.05
19 → 19	...	18 → 19	296350.0975	0.05
1 → 0	...	1 → 0	296832.6434	0.05
20 → 20	...	19 → 20	297465.7748	0.05
21 → 21	...	20 → 21	298640.4837	0.05
22 → 22	...	21 → 22	299874.6092	0.05
23 → 23	...	22 → 23	301168.7717	0.05
24 → 24	...	23 → 24	302523.3683	0.05
25 → 25	...	24 → 25	303939.1495	0.05
26 → 26	...	25 → 26	305416.2288	0.05
27 → 27	...	26 → 27	306955.5891	0.05
2 → 1	...	2 → 1	307708.933	0.05
28 → 28	...	27 → 28	308557.7006	0.05
29 → 29	...	28 → 29	310223.1553	0.05
30 → 30	...	29 → 30	311952.6045	0.05
31 → 31	...	30 → 31	313746.7254	0.05
32 → 32	...	31 → 32	315606.136	0.05
33 → 33	...	32 → 33	317531.628	0.05
34 → 34	...	33 → 34	319523.7022	0.05
35 → 35	...	34 → 35	321583.2829	0.05
36 → 36	...	35 → 36	323711.0603	0.05
37 → 37	...	36 → 37	325907.8061	0.05

$J' \rightarrow J''$	$K'_a \rightarrow K''_a$	$K'_c \rightarrow K''_c$	Frequency	Uncertainty
38 → 38	...	37 → 38	328174.2238	0.05
4 → 3	...	4 → 3	329297.017	0.05
39 → 39	...	38 → 39	330511.2308	0.05
40 → 40	...	39 → 40	332919.5466	0.05
41 → 41	...	40 → 41	335400.0193	0.05
42 → 42	...	41 → 42	337953.5045	0.05
43 → 43	...	42 → 43	340580.8008	0.05
44 → 44	...	43 → 44	343282.815	0.05
45 → 45	...	44 → 45	346060.4531	0.05
46 → 46	...	45 → 46	348914.536	0.05
6 → 5	...	6 → 5	350665.7242	0.05
47 → 47	...	46 → 47	351846.0103	0.05
48 → 48	...	47 → 48	354855.7624	0.05
49 → 49	...	48 → 49	357944.5602	0.05
50 → 50	...	49 → 50	361113.7051	0.05
7 → 6	...	7 → 6	361267.989	0.05
51 → 51	...	50 → 51	364363.823	0.05
52 → 52	...	51 → 52	367695.8741	0.05
53 → 53	...	52 → 53	371110.8241	0.05
8 → 7	...	8 → 7	371815.6563	0.05
54 → 54	...	53 → 54	374609.6343	0.05
55 → 55	...	54 → 55	378193.2503	0.05
56 → 56	...	55 → 56	381862.681	0.05
9 → 8	...	9 → 8	382308.8531	0.05
57 → 57	...	56 → 57	385618.666	0.05
58 → 58	...	57 → 58	389462.3422	0.05

$J' \rightarrow J''$	$K'_a \rightarrow K''_a$	$K'_c \rightarrow K''_c$	Frequency	Uncertainty
10 → 9	...	10 → 9	392747.739	0.05
59 → 59	...	58 → 59	393394.5349	0.05
60 → 60	...	59 → 60	397416.2236	0.05
61 → 61	...	60 → 61	401528.3889	0.05
11 → 10	...	11 → 10	403132.4641	0.05
63 → 63	...	62 → 63	410027.7134	0.05
12 → 11	...	12 → 11	413463.3194	0.05
64 → 64	...	63 → 64	414416.4654	0.05
65 → 65	...	64 → 65	418899.332	0.05
13 → 12	...	13 → 12	423740.4302	0.05
67 → 67	...	66 → 67	428150.584	0.05
14 → 13	...	14 → 13	433964.0481	0.05
16 → 15	...	16 → 15	454252.1454	0.05
17 → 16	...	17 → 16	464317.2314	0.05
18 → 17	...	18 → 17	474329.9039	0.05
19 → 18	...	19 → 18	484290.8339	0.05
21 → 20	...	21 → 20	504058.8884	0.05
22 → 21	...	22 → 21	513866.7739	0.05
23 → 22	...	23 → 22	523624.6008	0.05
24 → 23	...	24 → 23	533332.6979	0.05
25 → 24	...	25 → 24	542991.7623	0.05
26 → 25	...	26 → 25	552602.174	0.05
27 → 26	...	27 → 26	562164.6263	0.05
28 → 27	...	28 → 27	571679.7214	0.05
29 → 28	...	29 → 28	581147.9655	0.05
30 → 29	...	30 → 29	590570.0666	0.05

$J' \rightarrow J''$	$K'_a \rightarrow K''_a$	$K'_c \rightarrow K''_c$	Frequency	Uncertainty
31 $\rightarrow$ 30	...	31 $\rightarrow$ 30	599946.4946	0.05
32 $\rightarrow$ 31	...	32 $\rightarrow$ 31	609278.1882	0.05
33 $\rightarrow$ 32	...	33 $\rightarrow$ 32	618565.72	0.05
35 $\rightarrow$ 34	...	35 $\rightarrow$ 34	637011.4604	0.05
36 $\rightarrow$ 35	...	36 $\rightarrow$ 35	646171.0897	0.05
37 $\rightarrow$ 36	...	37 $\rightarrow$ 36	655289.64	0.05

## Isotopologues of HCCSH

The transition frequencies of each of the isotopologues of HCCSH are presented in Tables S3 to S6. The search for the isotopologues was based on empirical scaling of the rotational constants – having determined constants for HCCSH, the corresponding constants for each isotopologue can be estimated by scaling the *ab initio* prediction by the ratio between the *ab initio* and experimental constants for the normal species. For DCCSH, HCC<sup>34</sup>SH, and HCCSD we were able to measure at least the three lowest *a*-type transitions, with additional *b*-type transitions within reach with HCCSD. For the carbon-13 isotopologues, due to constraints on the sample mixture of carbon-13 acetylene, we were unable to measure the  $J = 3 - 2$  transition.

**Table S3: Transition frequencies for DCCSH. Frequencies and uncertainties are given in MHz.**

$J' \rightarrow J''$	$K'_a \rightarrow K''_a$	$K'_c \rightarrow K''_c$	Frequency	Uncertainty
1 $\rightarrow$ 0	0 $\rightarrow$ 0	1 $\rightarrow$ 0	10052.3895	0.002
2 $\rightarrow$ 1	...	2 $\rightarrow$ 1	20104.7671	0.002
3 $\rightarrow$ 2	...	3 $\rightarrow$ 2	30157.155	0.002

**Table S4: Centimeter wave transition frequencies of HCCSD. Frequencies and uncertainties are given in MHz. Uncertainties represent  $1\sigma$ , and correspond to the measurement method: 0.002 MHz for cavity measurements, and 0.15 MHz for DR experiments.**

$J' \rightarrow J''$	$K'_a \rightarrow K''_a$	$K'_c \rightarrow K''_c$	Frequency	Uncertainty
1 $\rightarrow$ 0	0 $\rightarrow$ 0	1 $\rightarrow$ 0	10721.6527	0.002
2 $\rightarrow$ 1	...	2 $\rightarrow$ 1	21443.0725	0.002
3 $\rightarrow$ 2	...	3 $\rightarrow$ 2	32164.0411	0.002
1 $\rightarrow$ 1	1 $\rightarrow$ 0	0 $\rightarrow$ 1	147150.2233	0.05
2 $\rightarrow$ 2	...	1 $\rightarrow$ 2	147345.6324	0.05
1 $\rightarrow$ 0	...	1 $\rightarrow$ 0	157676.0863	0.05
2 $\rightarrow$ 1	...	2 $\rightarrow$ 1	168201.3517	0.05
3 $\rightarrow$ 2	...	3 $\rightarrow$ 2	178628.4646	0.05

**Table S5: Transition frequencies for HCC<sup>34</sup>SH. Frequencies and uncertainties are in units of MHz.**

$J' \rightarrow J''$	$K'_a \rightarrow K''_a$	$K'_c \rightarrow K''_c$	Frequency	Uncertainty
1 $\rightarrow$ 0	0 $\rightarrow$ 0	1 $\rightarrow$ 0	10753.9826	0.002
2 $\rightarrow$ 1	...	2 $\rightarrow$ 1	21507.9047	0.002
3 $\rightarrow$ 2	...	3 $\rightarrow$ 2	32261.7034	0.002

**Table S6: Transition frequencies for the carbon-13 substituted isotopologues of HCCSH. Frequencies and uncertainties are in units of MHz.**

$J' \rightarrow J''$	$K'_a \rightarrow K''_a$	$K'_c \rightarrow K''_c$	Frequency	Uncertainty
H <sup>13</sup> C <sup>13</sup> SH				
1 $\rightarrow$ 0	0 $\rightarrow$ 0	1 $\rightarrow$ 0	10583.6475	0.002
2 $\rightarrow$ 1	...	2 $\rightarrow$ 1	21167.2373	0.002
HCC <sup>13</sup> SH				
1 $\rightarrow$ 0	0 $\rightarrow$ 0	1 $\rightarrow$ 0	10932.4782	0.002
2 $\rightarrow$ 1	...	2 $\rightarrow$ 1	21864.3829	0.002
H <sup>13</sup> C <sup>13</sup> CSH				
1 $\rightarrow$ 0	0 $\rightarrow$ 0	1 $\rightarrow$ 0	10538.5368	0.002
2 $\rightarrow$ 1	...	2 $\rightarrow$ 1	21077.0141	0.002



## Experimental constants of HCCSH isotopologues

Using the transition frequencies of the previous section, we were able to fit each isotopologue to a standard asymmetric top Hamiltonian. The results of the fits are presented in Table S7. Each fit used the equilibrium rotational constants calculated at the ae-CCSD(T)/cc-pCVQZ level, along with quartic centrifugal distortion constants obtained at the fc-CCSD(T)/ANO0 level. For all species except HCCSD where there was additional data collected from the  $b$ -type spectrum, the  $A$  rotational constant and centrifugal distortion terms were kept fixed at their *ab initio* values. Since only two lines were measured for the carbon-13 isotopologues, only the  $C$  rotational constant was fit.

**Table S7: Rotational constants of HCCSH isotopologues based on a  $S$ -reduction Hamiltonian in  $I^r$  representation. Values with parenthesis indicate  $1\sigma$  uncertainty, and were fit to the frequency data.**

Parameter	DCCSH	HCCSD	HCC <sup>34</sup> SH
$A$	295614.5503	152365.009(72)	292812.1687
$B$	–	5458.9339(215)	–
$C$	–	5262.7178(215)	–
$(B + C)/2$	5048.190416(268)	–	5431.245287(270)
$D_J \times 10^3$	1.00103709	1.189(48) <sup>a</sup>	1.266390
$D_{JK}$	0.1112897	0.133911	0.12423
$D_K$	21.9883	47.147	21.6206
No. Obs.	3	8	3
RMS <sup>b</sup>	14.69091	1.01251	0.10696
	H <sup>13</sup> CSSH	HC <sup>13</sup> CSH	H <sup>13</sup> C <sup>13</sup> CSH
$A$	295717.7538	295566.2348	293387.0117
$(B + C)/2$	5336.22170(45)	5513.34160(101)	5309.87368(45)
$D_J \times 10^3$	1.211640	1.311040	1.20972
$D_{JK}$	0.122557	0.12737	0.11881
$D_K$	21.4325	22.2746	22.4359
No. Obs.	2	2	2
RMS <sup>b</sup>	1.28636	7.31575	2.08619

<sup>a</sup> Fit to experimental data.

<sup>b</sup> Root-mean-squared error from the fit.

# Relative energetics of $[\text{H}_2\text{C}_2\text{S}]$ isomers

Table S8 gives the breakdown of the individual contributions used to calculate the relative energetics of  $[\text{H}_2\text{C}_2\text{S}]$  isomers. Electron correlation appears to be the largest difference between the three species: at the CCSD(T) level, a significantly larger amount of correlation is retrieved for c- $\text{H}_2\text{C}_2\text{S}$ , and the CCSDT(Q) contribution is approximately three times larger for HCCSH and c- $\text{H}_2\text{C}_2\text{S}$  compared to  $\text{H}_2\text{CCS}$ . This is an important factor in subsequent calculations of these molecules, as it suggests that an adequate treatment of correlation is necessary to describe them.

**Table S8: Breakdown of the energetic contributions for calculating the relative energies of the  $[\text{H}_2\text{C}_2\text{S}]$  isomers. Values are given in Hartrees.**

Contribution	$\text{H}_2\text{CCS}$	HCCSH	c- $\text{H}_2\text{C}_2\text{S}$
SCF/CBS	-474.431620	-474.410254	-474.375248
CCSD(T)/CBS <sup>a</sup>	-1.135513	-1.132691	-1.140461
MVD <sup>b</sup>	-1.143266	-1.143031	-1.143286
ZPE <sup>c</sup>	0.029453	0.027101	0.028931
DBOC	0.009483	0.009439	0.009458
(Q)	-0.000354	-0.000929	-0.000892
Total Energy	-476.671816	-476.650365	-476.621499

<sup>a</sup> Correlation contribution from the extrapolated ae-CCSD(T)/cc-pCVXZ (X = D, T, Q) energies

<sup>b</sup> Sum of the 1- and 2-electron mass-velocity terms

<sup>c</sup> Harmonic zero-point energy calculated with ae-CCSD(T)/cc-pCVQZ

## Vibration-rotation interaction constants of HCCSH

In order to determine a semi-experimental structure ( $r_e^{se}$ ) for HCCSH, we calculated vibration-rotation interaction constants to first order ( $\alpha_0$ ). These were calculated by using cubic force constants obtained at the fc-CCSD(T)/ANO0 level via finite differences of analytic second derivatives implemented in CFOUR. The constants are organized in Table S9.

**Table S9: First order vibration-rotation interaction constants ( $\alpha$ ) for each principal axis of HCCSH and its isotopologues. Constants are given in MHz.**

Species	$\alpha_A$	$\alpha_B$	$\alpha_C$
HCCSH	1677.439516	7.912688	13.037629
HCCSD	640.415181	6.375900	13.064239
DCCSH	1706.550707	5.410968	9.739249
H <sup>13</sup> C <sup>13</sup> CSH	1673.617558	7.723078	12.484151
HC <sup>13</sup> CSH	1656.285460	7.969615	13.034261
H <sup>13</sup> C <sup>13</sup> CSH	1651.334156	7.779594	12.490625
HCC <sup>34</sup> SH	1660.119835	7.663296	12.579400

## References

- (S1) Krantz, A.; Laureni, J. Characterization of matrix-isolated antiaromatic three-membered heterocycles. Preparation of the elusive thiirene molecule. *Journal of the American Chemical Society* **1981**, *103*, 486–496.